



US008216963B2

(12) **United States Patent**
Kibby et al.

(10) **Patent No.:** **US 8,216,963 B2**
(45) **Date of Patent:** **Jul. 10, 2012**

(54) **PREPARATION OF COBALT-RUTHENIUM
FISCHER-TROPSCH CATALYSTS**

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(*) Notice: Subject to any disclaimer, the term of this
patent is extended or adjusted under 35
U.S.C. 154(b) by 325 days.

(21) Appl. No.: **12/649,108**

(22) Filed: **Dec. 29, 2009**

(65) **Prior Publication Data**

US 2010/0174002 A1 Jul. 8, 2010

Related U.S. Application Data

(60) Provisional application No. 61/141,103, filed on Dec.
29, 2008.

(51) **Int. Cl.**
B01J 21/00 (2006.01)

(52) **U.S. Cl.** **502/260; 502/326; 502/66; 502/62;**
502/74; 502/87; 502/240; 502/255; 502/303;
502/313; 502/314; 502/327; 502/328; 502/330;
502/332; 502/336; 518/715; 518/714; 518/700;
518/717

(58) **Field of Classification Search** None
See application file for complete search history.

(56) **References Cited**

U.S. PATENT DOCUMENTS

4,492,774 A 1/1985 Kibby et al.
4,556,645 A 12/1985 Coughlin et al.
4,585,798 A 4/1986 Beuther et al.
4,605,676 A 8/1986 Kobylinski et al.
4,605,679 A 8/1986 Kobylinski et al.
4,670,414 A 6/1987 Kobylinski et al.
4,729,981 A 3/1988 Kobylinski et al.
4,822,824 A 4/1989 Iglesia et al.
4,913,799 A 4/1990 Gortsema et al.
5,036,032 A 7/1991 Iglesia et al.
5,114,563 A 5/1992 Lok et al.
5,128,377 A 7/1992 Behrmann et al.
5,140,050 A 8/1992 Mauldin et al.
5,168,091 A 12/1992 Behrmann et al.
5,198,203 A 3/1993 Kresge et al.
5,246,689 A 9/1993 Beck et al.
5,292,705 A 3/1994 Mitchell
5,334,368 A 8/1994 Beck et al.
5,424,264 A 6/1995 Richard et al.
5,466,646 A 11/1995 Moser
5,545,674 A 8/1996 Behrmann et al.
5,728,918 A 3/1998 Nay et al.
5,733,839 A 3/1998 Espinoza et al.
6,191,066 B1 2/2001 Singleton et al.

6,245,709 B1 6/2001 Clark et al.
6,262,131 B1 7/2001 Arcuri et al.
6,313,062 B1 11/2001 Krylova et al.
6,331,574 B1 12/2001 Lapidus et al.
6,331,575 B1 12/2001 Mauldin
6,465,529 B1 10/2002 Daage et al.
6,472,441 B1 10/2002 Kibby
6,491,880 B1 12/2002 Wang et al.
6,521,565 B1 2/2003 Clavenna et al.
6,531,517 B1 3/2003 Wachter et al.
6,649,662 B2 11/2003 Kibby
6,706,661 B1 3/2004 Krylova et al.
6,753,351 B2 6/2004 Clark et al.
7,045,486 B2 5/2006 Wang et al.
7,157,501 B2 1/2007 Steenwinkel et al.
7,300,959 B2 11/2007 Vogt et al.
7,361,619 B2 4/2008 Malek et al.
7,384,986 B2 6/2008 Huang et al.
2003/0149120 A1 8/2003 Wang et al.
2004/0171703 A1* 9/2004 Nay et al. 518/726
2004/0204504 A1 10/2004 Malek et al.
2007/0225383 A1 9/2007 Cortright et al.

FOREIGN PATENT DOCUMENTS

EP 153517 A1 9/1985
EP 0609079 8/1994
EP 1450950 6/2003
WO WO 96-04072 2/1996
WO WO 99-61550 12/1999
WO 00/61275 10/2000
WO WO 03-024905 3/2003

OTHER PUBLICATIONS

JP2005-104771, machine translation, 2005-USUi et al.*
International Search Report from PCT/US2009/069729.
International Examination Report from PCT/US2009/069729.
Beck, J.S. et al., A new family of mesoporous molecular sieves
prepared with liquid crystal templates., J. Am. Chem. Soc. 114,
10834-10843 (1992).
Kresge, et al., "Ordered mesoporous molecular sieves synthesized by
a liquid-crystal template mechanism" Nature 359:710-712 (1992).
U.S. Appl. No. 12/649,135, filed Dec. 29, 2009 entitled "Preparation
of Cobalt-Ruthenium/Zeolite Fischer-Tropsch Catalysts".
U.S. Appl. No. 12/343,534, filed Dec. 24, 2008 entitled "Zeolite
Supported Cobalt Hybrid Fischer-Tropsch Catalysts".

* cited by examiner

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(57) **ABSTRACT**

A method for forming a cobalt-containing Fischer-Tropsch
catalyst involves precipitating a cobalt oxy-hydroxycarbon-
ate species by turbulent mixing, during which a basic solution
collides with an acidic solution comprising cobalt. The
method further involves depositing the cobalt oxy-hydroxy-
carbonate species onto a support material to provide a catalyst
comprising cobalt and the support material. The support
material comprises one or more of alumina, silica, magnesia,
titania, zirconia, ceria-zirconia, and magnesium aluminate.

20 Claims, No Drawings

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PREPARATION OF COBALT-RUTHENIUM FISCHER-TROPSCH CATALYSTS

This application claims priority to U.S. Provisional Application Ser. No. 61/141,103 filed Dec. 29, 2008, which is incorporated herein by reference in its entirety. This application is related to a co-pending application entitled "Preparation of Cobalt-Containing Acidic Support-Based Fischer-Tropsch Catalysts" filed Dec. 29, 2009, which is incorporated herein by reference in its entirety.

FIELD OF ART

The present disclosure relates to a method for forming a cobalt-containing Fischer-Tropsch catalyst by precipitation of metal species through turbulent mixing and deposition of the precipitated species onto a support material comprising one or more of alumina, silica, magnesia, titania, zirconia, ceria-zirconia, and magnesium aluminate. The present disclosure also relates to a method of performing a Fischer-Tropsch synthesis reaction with the cobalt-containing Fischer-Tropsch catalyst.

BACKGROUND

Generally, precipitation or impregnation methods that add compounds of metal to preformed refractory supports (such as alumina or silica) are used to prepare small-particle, cobalt Fischer-Tropsch catalysts. During commercial production of these catalysts, precipitations on a large scale require aging conditions for the precipitate-support slurry that are the same as the precipitation conditions. However, precise control of process conditions is difficult.

Accordingly, there is a need for a method for forming a cobalt-containing Fischer-Tropsch catalyst which permits precise control of process conditions. There is also a need for a method for forming a cobalt-containing Fischer-Tropsch catalyst, which is highly active and has good selectivity for the formation of C₅+ hydrocarbons.

SUMMARY

Disclosed herein is a method for forming a cobalt-containing Fischer-Tropsch catalyst. The method comprises precipitating a cobalt oxy-hydroxycarbonate species by turbulent mixing, during which a basic solution collides with an acidic solution comprising cobalt. The method also comprises depositing the cobalt oxy-hydroxycarbonate species onto a support material to provide a catalyst comprising cobalt and the support material. The support material used herein is a conventional support material. The support material comprises one or more of alumina, silica, magnesia, titania, zirconia, ceria-zirconia, and magnesium aluminate.

Among other factors, the use of turbulent mixing to achieve precipitation can provide several advantages to the present catalyst forming method. Turbulent mixing can minimize blocking and fouling because it reduces contact of reactants with channel walls. Turbulent mixing can provide a high nucleation rate thereby generating extremely small precipitate particles. Furthermore, turbulent mixing can achieve almost instantaneous mixing. Precise control of process conditions (e.g. pH, temperature, flow rate, size of the support material, aging time, calcination conditions) is possible with turbulent mixing. Moreover, the use of turbulent mixing to precipitate a cobalt oxy-hydroxycarbonate species can provide highly active catalysts. For example, the use of turbulent mixing in the present method can provide a cobalt-containing

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Fischer-Tropsch catalyst with an activity about 30% to about 40% greater than a cobalt-containing Fischer-Tropsch catalyst produced without turbulent mixing by conventional methods.

Also disclosed herein is a method of performing a Fischer-Tropsch synthesis reaction. The method comprises forming a cobalt-containing Fischer-Tropsch catalyst by the method described herein and contacting the cobalt-containing Fischer-Tropsch catalyst with synthesis gas.

Among other factors, using the cobalt-containing Fischer-Tropsch catalyst produced by the method described herein, instead of a cobalt-containing Fischer-Tropsch catalyst produced without turbulent mixing by conventional methods, to produce Fischer-Tropsch hydrocarbons can provide a higher C₅+ hydrocarbon selectivity.

DETAILED DESCRIPTION

A. Definitions

The following terms appear throughout the specification and have the following meanings, unless otherwise indicated.

As used herein, "specific activity" refers to the rate of hydrocarbon production per unit weight of cobalt.

"Turbulent mixing" refers to mixing that uses the collision of two opposed high-speed jets of liquids to achieve ultrafast mixing. Due to the collision, a thin disk-shaped mixing zone is generated which bursts apart into very fine droplets. The droplets are transported to an exit port by an additional gaseous transport stream flowing perpendicular to the flow direction of the colliding jets.

"Volumetric activity" refers to the rate of hydrocarbon production per unit volume of catalyst.

B. Method for Forming a Cobalt-containing Fischer-Tropsch Catalyst

I. Precipitation and Deposition

In the presently disclosed methods for forming catalysts, a basic solution and an acidic solution comprising cobalt are mixed by turbulent mixing. Such turbulent mixing precipitates a cobalt oxy-hydroxycarbonate species. Thereafter, the methods involve depositing the cobalt oxy-hydroxycarbonate species onto a support material to provide a catalyst comprising cobalt and the support material.

The support material as used herein is a conventional support material. The support material comprises one or more of alumina, silica, magnesia, titania, zirconia, ceria-zirconia, and magnesium aluminate. The alumina, silica, magnesia, titania, zirconia, ceria-zirconia, and magnesium aluminate may be conventional or pyrogenic. Support materials that are pyrogenic (i.e. made in flames or plasmas) can provide catalysts with high specific activities. Pyrogenic alumina, silica, magnesia, and titania are generally porous and have a low density. Accordingly, these pyrogenic support materials tend to provide catalysts with average volumetric activities. However, pyrogenic zirconia, ceria-zirconia, and magnesium aluminate can provide catalysts with high specific activities and high volumetric activities (due to their high density) and their surface area is very stable. The support material may be precalcined. For example, precalcination of the support material at a temperature of about 600-800° C., for example, about 750° C., may be desirable.

Typically, as discussed above, turbulent mixing utilizes a gaseous transport stream such as air or nitrogen. An exemplary turbulent mixing device is manufactured by Ehrfeld Mikrotechnik BTS GmbH of Wendelsheim, Germany. In such a mixer, mixing takes place in a small volume, using air to create turbulence.

The mixer used for turbulent mixing can be equipped with micronozzles made from sapphire. Standard diameters of the nozzle openings are, for example, 50 and 100 μm , respectively. The body of the module can be made from Hastelloy.

Flow rates of the acidic solution, the basic solution, and the gaseous transport stream are sufficient to achieve turbulent mixing and will depend on size of the mixing zone. For example, flow rates of the acidic solution and the basic solution can be set to precipitate 200-250 mL of solution in about 15 minutes (e.g., on the order of 10 mL/min each). Flow rates can increase by several times in a larger continuous flow apparatus.

In one embodiment, depositing the cobalt oxy-hydroxycarbonate species onto the support material may involve injecting the cobalt oxy-hydroxycarbonate species into an aqueous slurry of the support material. The aqueous slurry of the support material may be well-stirred and hot. The aqueous slurry of the support material can be heated to a temperature of about 80-100° C., for example, about 90° C. Formation of the aqueous slurry of the support material, before precipitation, can increase the activity of the resulting catalyst.

In another embodiment, depositing the cobalt oxy-hydroxycarbonate species onto the support material may involve mixing the support material with either the acidic solution or the basic solution such that the cobalt oxy-hydroxycarbonate species precipitates (e.g., continuously precipitates) onto the support material.

The method may involve a single precipitation/deposition or multiple precipitation/deposition iterations with intervening decompositions. In an embodiment of the method involving a single precipitation/deposition, the catalyst may have a metal loading of ≤ 14 wt % Co, for example, ≤ 9 wt % Co to preserve sufficient specific activity. In an embodiment of the method involving multiple precipitation/deposition iterations, the intervening decompositions can advantageously open up pore volume, thereby permitting higher metal loadings while maintaining sufficient specific activity.

Following turbulent mixing, the resulting solution and precipitate can then be quickly conveyed to a larger volume containing slurried support material, where precipitate and support material are aged together (e.g., for 1 hour, at a temperature of about 80° C.). During aging, the precipitate re-dissolves and re-precipitates onto the support material. Aging generally increases the activity of the resulting catalyst by loading and dispersing cobalt onto the support material so that it is highly accessible to both H_2 and CO .

Aging in a large volume is beneficial on a commercial scale. Continuous aging in a large volume is also beneficial. With continuous aging, the aging volume can be advantageously large relative to the flow in and flow out, so that the flow out does not contain a significant amount of unreacted support and unreacted precipitate. In one embodiment, the aging volume is equal to or greater than the volume required to provide a residence time of an hour (i.e. equal to or greater than $60\times$ the flow rate entering/exiting the aging volume in mL/min). A process configuration having smaller turbulent mixing zones in parallel with the mixing zones' product directed into a large aging volume may be preferable.

The process may be a batch process, a continuous process, or a combination thereof. For example, precipitation, deposition, and aging may be continuous. If aging is continuous, the resulting solution and precipitate and a fresh feed of slurried support can enter the aging zone at a rate equal to aged slurry exiting the aging zone. Thereafter, the temperature of the aged slurry can be dropped to stop aging. The aged slurry can then be filtered batch-wise.

The acidic solution comprising cobalt may further comprise one or more of Re, Ru, Pt, Fe, Ni, Th, Zr, Hf, U, Mg, La, Au, Ag, Cu, Pd, Rh, Ir, Mn, and Cr. Thus, the catalyst forming method may deposit metal species in addition to the cobalt oxy-hydroxycarbonate species onto the support material. In particular, the Fischer-Tropsch catalysts formed by the presently disclosed method can contain an effective amount of cobalt and one or more of Re, Ru, Pt, Fe, Ni, Th, Zr, Hf, U, Mg, La, Au, Ag, Cu, Pd, Rh, Ir, Mn, and Cr on the support material. In general, the amount of cobalt present in the catalyst is between about 1 and about 50 weight percent, for example, between about 10 and about 30 weight percent, of the total catalyst composition. The catalysts can also contain basic oxide promoters such as ThO_2 , La_2O_3 , MgO , and TiO_2 , promoters such as ZrO_2 , noble metals (e.g. Pt, Pd, Ru, Rh, Os, Ir), coinage metals (e.g. Cu, Ag, Au), and other transition metals such as Fe, Mn, Ni, and Re.

The acidic solution may comprise cobalt (II) nitrate. The acidic solution may further comprise RuCl_3 or the nitrosyl nitrate salt of Ru. For example, the acidic solution may comprise $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O} + \text{Ru}(\text{NO})(\text{NO}_3)_3$, with a weight ratio of Co:Ru of between about 1:1 and about 400:1 (e.g. about 40:1), or $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O} + \text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O} + \text{Ru}(\text{NO})(\text{NO}_3)_3$, with a weight ratio of Co/Ru/La=about 40/1/1. Accordingly, a ruthenium-hydroxy species, as well as a lanthanum species, may be precipitated with the cobalt oxy-hydroxycarbonate species.

The basic solution may comprise K_2CO_3 or $(\text{NH}_4)_2\text{CO}_3$. The pH of the basic solution can be between about 7 and about 9. If the basic solution comprises K_2CO_3 , the pH can be about 9. If the basic solution comprises $(\text{NH}_4)_2\text{CO}_3$, the pH can be between about 7 and about 8. Setting the flow rates with a slight excess of the basic solution can provide these pH values. It has been discovered that ammonium carbonate generally provides catalysts with better activities and C_5+ hydrocarbon selectivities than potassium carbonate. Without wishing to be bound by any particular theory, it is believed that ammonium carbonate provides better results than potassium carbonate because ammonium carbonate redissolves more readily than potassium carbonate during aging, which better loads and disperses the cobalt oxy-hydroxycarbonate species onto the support material.

One embodiment involves heating the acidic solution and the basic solution. The acidic and basic solutions can be heated to a temperature of about 80-100° C., for example, about 80° C.

II. Drying

The catalyst comprising cobalt and the support material can be dried, for example, by freeze-drying (i.e., freezing in liquid nitrogen) followed by spray drying. A spray-freeze/freeze-dry process is described in Example 1 herein. The catalyst can also be oven dried (e.g., in an oven at 120° C. for 15 hours). The catalyst comprising cobalt and the support material may also be spray dried, for example, to provide a fluidized bed catalyst or a slurry catalyst. If the basic solution comprises K_2CO_3 , the catalyst must be thoroughly washed before drying in order to completely remove residual potassium.

III. Conditioning/Activation Procedures

a. Generally

Conditioning/activation serves to provide metals in their zero-valent form, increases the metal loading and/or increases the metal dispersion on the support material. Metals are present in cationic form when precipitated onto the support material. However, metals in cationic form are inactive for Fischer-Tropsch synthesis. An effective Fischer-Tropsch catalyst requires metals in their zero-valent (i.e. metallic)

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form. An effective Fischer-Tropsch catalyst also requires a high metal loading and/or a high metal dispersion to provide a highly accessible metal surface area to both H₂ and CO. Metal dispersion decreases with increased metal loading so a balance is necessary.

Aging as discussed above serves to condition/activate the catalyst. Additional conditioning/activation steps are discussed below.

b. Decomposition

The catalyst comprising cobalt and the support material may also be subjected to decomposition to decompose the cobalt oxy-hydroxycarbonate species. Decomposition refers to the separation of a chemical compound and is known in the art. In the method described herein, the cobalt oxy-hydroxycarbonate species decomposes into cobalt oxyhydroxides. It has been discovered that decomposition by heating to about 200° C. in an oxidizing environment, inert gas or a reducing environment, before further calcination, can advantageously increase activity.

c. Calcination

The catalyst comprising cobalt and the support material may be calcined. Calcination is known in the art. Calcination converts metal salts to their (dry) oxide form thereby decreasing water content for subsequent reduction. Water is undesirable during reduction because water raises the reduction temperature increasing the chances of undesirably sintering the metallic crystallites. It has been discovered that calcination at an intermediate temperature (e.g. about 250-350° C., for example, about 300° C.) can advantageously increase activity. For example, calcining the catalyst comprising cobalt and the support material can be performed in a fluidized (i.e., moving) bed at a temperature of about 250-350° C., for example, about 300° C., for about 2-16 hours, for example, about 8 hours.

d. Reduction

The catalyst comprising cobalt and the support material may be reduced. Reduction is known in the art. Reduction converts the cobalt oxyhydroxides into cobalt crystallites in zero-valent form to provide an effective Fischer-Tropsch catalyst. The catalyst should be reduced slowly enough to avoid sintering the metallic crystallites. For example, the catalyst can be heated at a rate of $\leq 1^\circ \text{C./min}$ while maintaining vapor pressure below about 1% atmospheric pressure. The catalyst comprising cobalt and the support material can be reduced in a fast flow of hydrogen at a temperature of about 350-400° C., for example, about 350° C., for about 8-16 hours, for example, about 12 hours. A temperature of about 350-400° C. is particularly advantageous because it completes reduction (i.e. >95%) in a reasonable time while avoiding sintering of the metallic crystallites.

e. Reoxidation

After reduction, the catalyst comprising cobalt and the support material may be reoxidized. Oxidation is known in the art. Upon reoxidation, the cobalt is in an oxide state different from the oxide state after calcination. After reoxidation, the catalyst can be reduced at temperatures about 100-150° C. lower than those required for the initial reduction. Re-oxidation may occur at a temperature of about 200-300° C., for example, about 300° C., in air. Reoxidation and subsequent reduction are desirable, but not necessary, because the catalyst is active after the initial reduction. If reoxidation occurs, it preferably does not occur at higher than about 300° C. because temperatures higher than about 300° C. can cause a significant decrease in activity.

f. Second Reduction

If the catalyst is reoxidized, a second reduction converts the cobalt oxyhydroxides into cobalt crystallites in zero-valent

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form to provide an effective Fischer-Tropsch catalyst. The catalyst can be reduced at temperatures of from about 200° C. to about 350° C., for example, from about 200° C. to about 260° C. This lower temperature range can be advantageous in a large reactor system. The general sequence of reduction, reoxidation, and a second reduction (i.e. ROR) is known in the art. For example, the general sequence of reduction, reoxidation, and a second reduction is disclosed in U.S. Pat. Nos. 4,605,676 and 4,729,981, which patents are incorporated herein by reference in their entirety.

g. Passivation

The catalyst comprising cobalt and the support material may be passivated between reduction and re-oxidation and/or after the second reduction. In particular, passivation after a second reduction is useful if the catalyst is activated in a reactor separate from the Fischer-Tropsch reactor. If the catalyst is activated in situ, passivation after a second reduction is not required and synthesis gas may be introduced to the Fischer-Tropsch reactor directly after the second reduction. Passivation is known in the art. In the present method, passivation typically covers the Co atoms on the metal surfaces with 1-2 atoms of O. At this point in the method, cobalt is well-dispersed on the support material (e.g. the support material comprises 20 wt % Co) and is extremely pyrophoric. Accordingly, it has been discovered that passivation in dilute air or with a limited air flow is advantageous. For example, passivation can comprise first purging with inert gas at reduction temperature, then cooling to ambient temperature (e.g., <50° C.), then passing nitrogen-diluted air (e.g., 1% O₂) over the catalyst.

C. Method of Performing a Fischer-Tropsch Synthesis Reaction

The cobalt-containing Fischer-Tropsch catalyst formed by the presently disclosed methods can be used to make heavy gasoline- and diesel-range hydrocarbons. The Fischer-Tropsch catalyst converts synthesis gas to linear hydrocarbons corresponding to a Schulz-Flory distribution.

Accordingly, the method of performing a Fischer-Tropsch synthesis reaction comprises forming a cobalt-containing Fischer-Tropsch catalyst according to the method described herein and contacting the cobalt-containing Fischer-Tropsch catalyst with synthesis gas.

Ideally, a Fischer-Tropsch catalyst should have high synthesis activity and chain-growth probability, with little to no deactivation of the synthesis functionality in a hydrothermal, reducing atmosphere. The cobalt-containing Fischer-Tropsch catalyst formed by the presently disclosed methods can exhibit both high activity and good selectivity for the formation of C₅+ hydrocarbons. In one embodiment, the method of performing a Fischer-Tropsch synthesis reaction includes converting the synthesis gas to hydrocarbon products with a C₅+ hydrocarbon selectivity of \geq about 80%, for example, \geq about 90%.

The Fischer-Tropsch synthesis process converts a variety of hydrocarbonaceous resources (e.g. biomass, natural gas, coal, shale oil, petroleum, refinery fuel gas, tar sands, oil shale, municipal waste, agricultural waste, forestry waste, wood, shale oil, bitumen, crude oil, fractions from crude oil, and combinations thereof) into hydrocarbon products typically obtained from petroleum. To prepare hydrocarbons via the Fischer-Tropsch process, one of these feedstocks is first converted into synthesis gas. The synthesis gas is further processed into syncrude by the Fischer-Tropsch process. Syncrude prepared from the Fischer-Tropsch process comprises a mixture of various solid, liquid, and gaseous hydrocarbons.

In Fischer-Tropsch chemistry, syngas is converted to liquid hydrocarbons by contact with a Fischer-Tropsch catalyst under reactive conditions. Typically, methane and optionally heavier hydrocarbons (i.e. ethane and heavier) are sent through a conventional syngas generator to provide synthesis gas. Generally, synthesis gas contains hydrogen and carbon monoxide, and may include minor amounts of carbon dioxide and/or water. The presence of sulfur, nitrogen, halogen, selenium, phosphorus and arsenic contaminants in the syngas is undesirable. For this reason and depending on the quality of the syngas, sulfur and other contaminants may be removed from the feed before performing the Fischer-Tropsch chemistry. Means for removing these contaminants are well known to those of skill in the art. For example, ZnO guard beds may be used to remove sulfur impurities. It also may be desirable to purify the syngas prior to the Fischer-Tropsch reactor to remove carbon dioxide produced during the syngas reaction and any additional sulfur compounds not already removed. This can be accomplished, for example, by contacting the syngas with a mildly alkaline solution (e.g., aqueous potassium carbonate) in a packed column.

In the Fischer-Tropsch process, contacting a synthesis gas comprising a mixture of H₂ and CO with a Fischer-Tropsch catalyst under suitable temperature and pressure reactive conditions forms liquid, gaseous, and solid hydrocarbons. The Fischer-Tropsch reaction over cobalt is typically conducted at temperatures of about 165° C. to about 250° C., optionally about 205° C. to about 240° C.; pressures of about 10-600 psia (0.7-41 bar), optionally about 75-350 psia (5-25 bar); and catalyst space velocities of about 100-10,000 cc/g/hr, optionally about 300-3,000 cc/g/hr. Conditions for performing Fischer-Tropsch type reactions are well known to those of skill in the art.

The products of the Fischer-Tropsch synthesis process may range from C₁ to C₂₀₀₊ with a majority in the C₅ to C₁₀₀₊ range. The reaction can be conducted in a variety of reactor types, such as fixed bed reactors containing one or more catalyst beds, slurry reactors, fluidized bed reactors, or a combination of different type reactors. Such reaction processes and reactors are well known and documented in the literature. In one embodiment, the synthesis gas contacts the cobalt-containing Fischer-Tropsch catalyst in a fluidized bed reactor or a slurry reactor.

The slurry Fischer-Tropsch process utilizes superior heat and mass transfer characteristics for the strongly exothermic synthesis reaction and is able to produce relatively high molecular weight, paraffinic hydrocarbons when using a cobalt catalyst. In the slurry process, a syngas comprising a mixture of hydrogen and carbon monoxide is bubbled up as a third phase through a slurry which comprises a particulate Fischer-Tropsch type hydrocarbon synthesis catalyst dispersed and suspended in a slurry liquid comprising hydrocarbon products of the synthesis reaction which are liquid under the reaction conditions. The mole ratio of the hydrogen to the carbon monoxide may broadly range from about 0.5 to about 4, but is more typically within the range of from about 0.7 to about 2.75 and optionally from about 0.7 to about 2.5. An example of a useful Fischer-Tropsch process is taught in EP 0609079, which is completely incorporated herein by reference for all purposes.

Fischer-Tropsch catalysts can provide chain growth probabilities that are relatively low to moderate, with the reaction products including a relatively high proportion of low molecular weight C₂₋₈ olefins and a relatively low proportion of high molecular weight C₃₀₊ waxes, or relatively high chain growth probabilities, with the reaction products including a

relatively low proportion of low molecular weight C₂₋₈ olefins and a relatively high proportion of high molecular weight C₃₀₊ waxes.

Except for the light, mainly gaseous fraction, the product from a Fischer-Tropsch process contains predominantly paraffins. The products from Fischer-Tropsch reactions generally include a light reaction product and a waxy reaction product. The light reaction product (i.e., the condensate fraction) includes hydrocarbons boiling below about 371° C. (e.g., tail gases through middle distillate fuels), largely in the C₅-C₂₀ range, with decreasing amounts up to about C₃₀. The waxy reaction product (i.e., the wax fraction) includes hydrocarbons boiling above about 316° C. (e.g., vacuum gas oil through heavy paraffins), largely in the C₂₀₊ range, with decreasing amounts down to C₁₀.

Both the light reaction product and the waxy product are substantially paraffinic. The waxy product generally comprises greater than 70 weight % normal paraffins, and often greater than 80 weight % normal paraffins. The light reaction product comprises not only paraffinic products, but also a significant proportion of alcohols and olefins. In some cases, the light reaction product may comprise as much as 50 weight %, or even higher, alcohols and olefins.

The following examples are provided to further illustrate the present methods and advantages thereof. The examples are meant to be only illustrative, and not limiting.

EXAMPLES

Example 1

Synthesis of Catalyst 1

Precipitation and Deposition

A cobalt-ruthenium-lanthana Fischer-Tropsch catalyst was made by precipitating the three components from an acidic nitrate solution onto a gamma-alumina support (ALCOA HiQ-7000 series, 30-70 μm) using a basic carbonate solution. The support was calcined at 750° C. in air for three hours immediately prior to use. It was then slurried in distilled water and heated to ≦80° C. in an open receiving vessel that was large enough to accommodate influx of reactant solutions. The slurry was stirred vigorously throughout the precipitation itself and also during subsequent aging. The nitrate solution contained cobalt, ruthenium and lanthanum in a 40:1:1 weight ratio and was also kept at 80° C. or hotter. Cobalt and lanthanum were added as the hydrated nitrate salts, while ruthenium nitrosyl nitrate was the ruthenium source. Representative quantities in the nitrate solution, the carbonate solution, and the alumina support were as follows.

Nitrate solution: 133 mg RuCl₃ (or an equivalent amount of the nitrosyl nitrate salt), 338 mg La(NO₃)₃·6H₂O, and 15.272 g Co(NO₃)₂·6H₂O were dissolved in 130 mL distilled water.

Carbonate solution: 5.95 g (NH₄)₂CO₃ was dissolved in another 130 mL to make a 0.48M solution.

Alumina support: 10 g of precalcined alumina was suspended in 50 mL distilled water.

The carbonate solution and the nitrate solution, both at ≦80° C., were fed at flow rates of about 40 mL/min via peristaltic pumps to two of the inlets of a turbulent mixing volume about 1 mm in diameter. The mixing zone had three inlets and one outlet. A flow of about 6 mL (STP)/min nitrogen was fed to the other inlet to keep the mixing volume well agitated. The nitrogen inlet pressure was about 0.5 atm above ambient pressure. Relative concentrations and/or flow rates of the basic and acidic solutions were adjusted to maintain pH=7-8 in the turbulent zone. This was more precise than

trying to control the pH through feedback from the pH measurement itself. The slurry of fresh precipitate passed immediately through the mixing volume outlet and directly into the suspension containing the support. It was delivered there within a second of being formed.

Enough precipitate slurry was passed into the support suspension to reach the target concentration levels on the catalyst. The amount of catalyst components added per 10 g of alumina were 2.55 g Co metal, 0.065 g Ru metal, and 0.125 g lanthanum oxide. The finished catalyst compositions were then 20 wt % Co, 0.5 wt % Ru, 1 wt % La_2O_3 and 78.5 wt % alumina. These catalysts were made with a single precipitation step, but specific catalyst activities declined slightly above 9 wt % Co and rapidly above 14 wt % Co for catalysts made this way. Higher specific activities for the high metal loadings would require multiple precipitations, each contributing a fraction of the target loading, with intervening decompositions of the metal oxy-hydroxycarbonate species in order to open up pore volume. After the reaction solution flows were stopped, the catalyst suspension was aged for ten minutes to an hour at 80° C. or above, with constant stirring. The catalyst solids were then filtered from the suspension and washed thoroughly. This batch process could be converted into a continuous one by addition of large volume reservoirs for the reactant solutions and two or more holding tanks in series for aging the precipitated catalyst.

Treatments

Spray-Freezing/Freeze Dry

The damp catalyst solids were reslurried in distilled water and sprayed into liquid nitrogen via an injector similar to those used in automobiles to inject fuels into cylinders. Pulses of the slurry were sprayed at timed intervals that allowed the liquid nitrogen to almost quit boiling after each injection. Depending on the solids content in the slurry, sizes of the mainly spherical, frozen catalyst could be varied from about one millimeter in diameter to several millimeters. The frozen particles were then transferred to a freeze-dry apparatus where they were dried under vacuum while still frozen. This procedure produced uniform, porous catalyst particles using very small quantities of material; it is referred to herein as the "spray-freeze/freeze dry" (SFFD) process. The SFFD process is described in EP 1450950, the contents of which are incorporated herein in their entirety. For larger scales, a conventional spray drying process would produce large quantities of 100 μm -sized particles.

Conditioning/Activation

Decomposition: The SFFD-formed catalyst was then heated in a gently moving bed (a modified rotary evaporator) under a flow of 10% H_2 in nitrogen to 200° C. This decomposed the metal oxy-hydroxycarbonate species to metal oxyhydroxides.

150 mg catalyst samples (30 mg Co, ca 0.8 mg Ru) sized to 125-160 μm particle size, were diluted three times by volume with corundum particles having similar sizes and were loaded into one of sixteen 3.6 mm ID reactors in a multireactor test unit. They were conditioned and activated at 2 atm pressure, which was the pressure required to reliably obtain all the required treatment flows against a vent pressure of 1 atm.

In Example 1, the catalyst was subjected to the further conditioning/activation treatment described below through initial reduction and passivation. Catalyst 1 refers to the catalyst formed by the process of Example 1.

Drying and Calcination: First, the samples were heated at 1° C./min to 120° C. in dry air at a flow of 15.6 sccm (GHSV (i.e. gaseous hourly space velocity) per catalyst about 1000 h^{-1} , total GHSV about 250 h^{-1}) and held at that temperature for 3 hours, then were heated again in the same air flow at 1°

C./min to 300° C. and held at that temperature for 9 hours. The heating was then stopped and the samples were allowed to cool ballistically. The temperature decreased to 200° C. in about one-half hour and 100° C. in about three hours. When it reached 50° C., the air flow was replaced by an equal flow of nitrogen to purge the catalyst and lines of oxygen.

Reduction and Passivation: The samples were next switched to a 25 sccm flow of hydrogen after the nitrogen purge had continued for about one-half hour (GHSV per catalyst about 1500 h^{-1} , total GHSV about 375 h^{-1}). The samples were then heated at 1° C./min to 350° C. in the hydrogen flow and held at that temperature for 15 hours. They were then cooled linearly at about 0.4° C./min to a little above 50° C., where cooling became limited to even slower rates. At that point, the hydrogen was replaced by a nitrogen flow of 8.3 sccm (GHSV per catalyst about 500 h^{-1} , total GHSV about 125 h^{-1}). The catalyst was held in the nitrogen flow for about 3 hours and cooled to about 40° C. The nitrogen flow was slowly replaced by a similar air flow and the catalyst was held in the air flow for 10 hours. If diluted air (ca 2% O_2) is used, the passivation step can start at a higher temperature (about 100° C.).

Reoxidation: The reduced and passivated samples were then heated in air at 1° C./min to 300° C., held at that temperature for 7 hours, and then cooled ballistically as in the initial calcination. The same air flow was also used (15.6 sccm=GHSV per catalyst about 1000 h^{-1} , total GHSV about 250 h^{-1}). This temperature is about the highest that can reliably be used before some solid state reaction of cobalt oxides with alumina occurs.

Second Reduction and Passivation: The samples were again reduced with a temperature-time profile, gas flows, and switching times identical to those in the first reduction. Ruthenium and cobalt are alloyed at this point and present in oxide particles that interact much less with the alumina support than the initial monolayer. Thus, the catalysts are much easier to reduce. A maximum temperature of 250° C. is sufficient, and a lower hydrogen concentration (5%-10% hydrogen in nitrogen) may be used. For these samples, final reductions were at 1° C./min to 350° C. with a ten hour hold.

Example 2

Synthesis of Catalyst 2

A catalyst was prepared as in Example 1 with the following exceptions. After SFFD, the catalyst was heated to 200° C. in air in a fluidized bed to decompose the metal oxy-hydroxycarbonate species. Thereafter, it was transferred to an activation unit where it was conditioned and activated as in Example 1. Catalyst 2 refers to the catalyst formed by the process of Example 2.

Example 3

Synthesis of Catalyst 3

A catalyst was prepared as in Example 1 with the following exceptions. After SFFD, the catalyst was transferred to a fixed-bed test reactor where it was conditioned and activated by the full activation treatment described in Example 1. Catalyst 3 refers to the catalyst formed by the process of Example 3.

Example 4

Synthesis of Catalyst 4

A catalyst was prepared as in Example 3 with the following exceptions. Immediately following SFFD, the catalyst was

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transferred to a shallow bed in an open oven and dried at 120° C. in air. The catalyst was then transferred to a test reactor where it was conditioned and activated by the full activation treatment described in Example 1. Catalyst 4 refers to the catalyst formed by the process of Example 4.

Example 5

Synthesis of Catalyst 5

A catalyst was prepared as in Example 1 with the following exceptions. The basic carbonate solution was a potassium carbonate solution rather than an ammonium carbonate solution. Representative quantities in the carbonate solution were as follows. Carbonate solution: 8.55 g K₂CO₃ was dissolved in another 130 mL to make a 0.48 M solution. Also, relative concentrations and/or flow rates of the basic and acidic solutions were adjusted to maintain pH=9. The solutions and catalyst slurry were maintained near boiling (95° C.). The amounts of catalyst components added per 10 g alumina were also different. After filtering the catalyst solids, the filter cake was washed thoroughly with hot (>80° C.) water, re-slurried in distilled water and filtered again. Washing, re-slurrying, and re-filtering were repeated until no trace of potassium was detected in the wash water.

The catalyst was oven dried at 120° C. for 4 hours. The dry catalyst was then subjected to the conditioning/activation treatment as in Example 1 with the following exceptions. The catalyst was calcined in air to 300° C. with a 2 hour hold. The catalyst was reduced in hydrogen to 350° C. with at least a 5 hour hold. Catalyst 5 refers to the catalyst formed by the process of Example 5.

Comparative Example 6

Synthesis of Comparative Catalyst 6

A catalyst was prepared as in Example 5 with the following exceptions. The turbulent mixing volume was omitted. Instead, the reactant solutions were delivered directly to the receiving vessel. Comparative Catalyst 6 refers to the catalyst formed by the process of Comparative Example 6.

Example 7

Synthesis Gas Conversion with Catalysts 1-5 and Comparative Catalyst 6

Catalysts 1-5 and Comparative Catalyst 6 were tested for synthesis gas conversion as follows. The synthesis gas conversion tests were carried out in the same reactors used for conditioning and activation. The temperature was reduced to 190° C. and the pressure of hydrogen was increased to 10 atm. A flow of 2 L/h per reactor of synthesis gas with a H₂/CO mole ratio of 2 was initiated. After a 100 hour breaking in period, the temperature was increased in 10° C. steps to a maximum of 240° C., which was the limit for effective temperature control. Pressure and H₂/CO ratio, respectively, were also varied in some experiments from 10 to 20 atm and from 1.6 to 2.0, respectively. H₂, CO, CO₂, and hydrocarbon products up to C₁₃H₂₈ were analyzed online by gas chromatography. Hot traps at 150° C. collected C₁₃+ hydrocarbons. These were drained periodically and the C₁₃+ hydrocarbons were weighed and analyzed offline, also by gas chromatography. Run periods were 50-100 hours at each condition to allow equilibration and collection of representative samples.

As shown in Tables 1 and 2, the synthesis gas conversion activities and hydrocarbon selectivities for Catalysts 1 and 2 are nearly identical. Thus, it doesn't matter whether decom-

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position of the oxy-hydroxycarbonate species occurs in air or in a reducing environment. The activities at 240° C. shown in Table 1 are too high to be controlled in conventional fixed bed reactors. Fluidized bed or slurry reactors capable of managing the heat release would be needed. Selectivities to C₅+ hydrocarbons were 80% or greater at 240° C. and H₂/CO=1.6 and close to 90% at lower temperatures.

TABLE 1

Activities of Catalysts 1 and 2 at 10 atm, 200-600 h Onstream					
Catalyst		Activity, gCH ₂ /h/mL		Activity, gCH ₂ /h/g _{C_o}	
		1	2	1	2
T, ° C.	H ₂ /CO	Decomp.	Decomp.	Decomp.	Decomp.
210	2.0	0.041	0.040	1.27	1.26
230	2.0	0.127	0.127	3.97	3.97
230	1.6	0.100	nm	3.14	nm
240	1.6	0.149	0.147	4.7	4.6
240	2.0	0.19	0.19	5.9	5.8
	est.				

*Decomp. refers to decomposition of metal oxy-hydroxycarbonate species

TABLE 2

Hydrocarbon Selectivities for Catalysts 1 and 2 at 10 atm, 200-600 h Onstream		
	Catalyst	
	1	2
230° C., H ₂ /CO = 2.0		
C ₁ -C ₄	20%	22%
C ₅ -C ₁₂	34%	37%
C ₁₃ +	46%	41%
240° C., H ₂ /CO = 1.6		
C ₁ -C ₄	16%	17%
C ₅ -C ₁₂	36%	37%
C ₁₃ +	48%	46%

As shown in Tables 3 and 4, SFFD followed by the full activation treatment for Catalyst 3 provided only slightly better activity than did the SFFD followed by oven drying at 120° C. and then the full activation treatment for Catalyst 4. Furthermore, the C₅+ selectivity for Catalyst 3 was about 5% lower at 240° C. and H₂/CO=2, so much of the extra product was light hydrocarbons.

TABLE 3

Activities of Catalysts 3 and 4 at 10 atm, >750 h Onstream			
	Catalyst		Ratio, 3/4
	3	4	
	SFFD	SFFD, OD*	
GHSV, h ⁻¹	1250	1200	
240° C., H ₂ /CO = 2			
Activity, gCH ₂ /h/mL	0.17	0.14	1.22
Activity, gCH ₂ /h/g _{C_o}	5.6	4.6	

*SFFD, OD refer to spray-freeze/freezing-drying and oven drying, respectively

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TABLE 4

Hydrocarbon Selectivities for Catalysts 3 and 4 at 10 atm, >750 h Onstream		
	Catalyst	
	3	4
GHSV, h ⁻¹ 240° C., H ₂ /CO = 2	1250	1200
C ₁ -C ₄	30%	25%
C ₅ -C ₁₂	42%	41%
C ₁₃ +	28%	34%

Tables 5 and 6 list activities and selectivities for Catalyst 5 and Comparative Catalyst 6, which were made with potassium carbonate. Table 5 shows that Catalyst 5, produced with turbulent mixing, is 30-40% more active than Comparative Catalyst 6, produced in a conventional manner without turbulent mixing. Table 6 shows that Catalyst 5 also produced about 2% more C₅+ than Comparative Catalyst 6. In general, catalysts produced with potassium carbonate were both less active and less selective for C₅+ hydrocarbons than catalysts produced with ammonium carbonate.

TABLE 5

Activities of Catalyst 5 and Comparative Catalyst 6 at 10 atm, H ₂ /CO = 2, >350 h Onstream			
	Catalyst		
	5 turbulent	Comparative Catalyst 6 conventional	Ratio, 5/Comparative Catalyst 6
GHSV, h ⁻¹ 230° C.	1120	1180	
Activity, gCH ₂ /h/mL	0.072	0.053	1.38
Activity, gCH ₂ /h/gCo 240° C.	2.41	1.75	
Activity, gCH ₂ /h/mL	0.098	0.073	1.35
Activity, gCH ₂ /h/gCo	3.26	2.42	

TABLE 6

Selectivities for Catalyst 5 and Comparative Catalyst 6 at 10 atm, H ₂ /CO = 2, >350 h Onstream		
	Catalyst	
	5	Comparative Catalyst 6
GHSV, h ⁻¹ 230° C.	1120	1180
C ₁ -C ₄	28%	30%
C ₅ -C ₁₂	37%	38%
C ₁₃ +	35%	32%
C ₁ -C ₄ 240° C.	32%	34%
C ₅ -C ₁₂	38%	38%
C ₁₃ +	30%	28%

While various embodiments have been described, it is to be understood that variations and modifications may be resorted

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to as will be apparent to those skilled in the art. Such variations and modifications are to be considered within the purview and scope of the claims appended hereto.

5 What is claimed is:

1. A method for forming a cobalt-containing Fischer-Tropsch catalyst, comprising:

precipitating a cobalt oxy-hydroxycarbonate species by turbulent mixing, wherein a basic solution is collided

10 with an acidic solution comprising cobalt; and

depositing the cobalt oxy-hydroxycarbonate species onto a support material to provide a catalyst comprising cobalt and the support material, wherein the support material comprises one or more of alumina, silica, magnesia, titania, zirconia, ceria-zirconia, and magnesium aluminate.

2. The method of claim 1, wherein depositing the cobalt oxy-hydroxycarbonate species onto the support material comprises injecting the cobalt oxy-hydroxycarbonate species into an aqueous slurry of the support material.

3. The method of claim 1, wherein depositing the cobalt oxy-hydroxycarbonate species onto the support material comprises mixing the support material with either the acidic solution or the basic solution such that the cobalt oxy-hydroxycarbonate species is precipitated onto the support material.

4. The method of claim 1, further comprising multiple precipitation/deposition iterations with intervening decompositions.

5. The method of claim 1, further comprising spray drying the cobalt-containing Fischer-Tropsch catalyst to provide a fluidized bed catalyst or a slurry catalyst.

6. The method of claim 1, wherein the acidic solution and the basic solution are heated.

7. The method of claim 6, wherein the acidic solution and the basic solution are heated to a temperature of about 80° C.

8. The method of claim 1, wherein the acidic solution comprises cobalt (II) nitrate.

9. The method of claim 1, wherein the acidic solution further comprises one or more metals selected from the group consisting of Re, Ru, Pt, Fe, Ni, Th, Zr, Hf, U, Mg, La, Au, Ag, Cu, Pd, Rh, Ir, Mn, and Cr.

10. The method of claim 9, wherein the acidic solution comprises Co(NO₃)₂*6H₂O+Ru(NO)(NO₃)₃.

11. The method of claim 10, wherein the acidic solution has a weight ratio of Co:Ru between about 1:1 and about 400:1.

12. The method of claim 11, wherein the acidic solution further comprises La(NO₃)₃*6H₂O and has a weight ratio of Co/Ru/La=about 40/1/1.

13. The method of claim 1, wherein the basic solution comprises K₂CO₃ or (NH₄)₂CO₃ and has a pH of about 7 to about 9.

14. The method of claim 1, further comprising decomposing the oxy-hydroxycarbonate species at about 200° C. in an oxidizing environment, inert gas, or a reducing environment.

15. The method of claim 14, further comprising calcining the catalyst comprising cobalt and the support material at a temperature of about 250° C. to about 350° C.

16. The method of claim 1, further comprising reducing the catalyst comprising cobalt and the support material at a temperature of about 350° C. to about 400° C.

17. The method of claim 16, further comprising re-oxidizing the catalyst comprising cobalt and the support material at ≅ about 300° C.

18. The method of claim 17, further comprising reducing the catalyst comprising cobalt and the support material for a second time.

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19. The method of claim **18**, further comprising passivating the catalyst comprising cobalt and the support material between reducing and re-oxidizing and/or after reducing for a second time.

20. A method of performing a Fischer-Tropsch synthesis reaction, comprising: 5

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forming a cobalt-containing Fischer-Tropsch catalyst according to the method of claim **1**; and contacting the cobalt-containing Fischer-Tropsch catalyst with synthesis gas.

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